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(71)Applicant : MITSUBISHI CHEMICALS CORP

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(72)Inventor : TAKEDA MASAYUKI  
TAKAHASHI TAKAKO  
TAKEHARA MASAHIRO  
UE MAKOTO

(54) METHOD FOR PURIFYING FLUORO COMPLEX SALT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for obtaining high-purity fluoro complex salt in high yield by a simple operation.

SOLUTION: This method for purifying a fluoro complex salt represented by the general formula (I)  $Q^+MF_n^-$  [wherein  $Q^+$  represents an organic ionium ion or a metal ion; M represents an element of the group 4-16 of the periodic table; and (n) is an integer of 3 to 7] is characterized by extracting the above fluoro complex salt by using an organic solvent which dissolves the above fluoro complex salt and does not dissolve contaminants from a mixture containing the above fluoro complex salt and these contaminants.

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## CLAIMS

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[Claim(s)]

[Claim 1] A refining method of fluoro complex salt extracting said fluoro complex salt from a mixture containing fluoro complex salt and impurity which are shown by following general formula (I) using an organic solvent which dissolves said fluoro complex salt and does not dissolve said impurity.

[Formula 1]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

[Claim 2] The refining method according to claim 1 with which an organic solvent is chosen from alcohol, halogenated alkane, acetonitrile, and chain carboxylate and which is a kind at least.

[Claim 3] The refining method according to claim 1 or 2 whose M is periodic table 5 fellows' element in formula (I) and whose n is 6.

[Claim 4] The refining method according to any one of claims 1 to 3 whose  $Q^+$  is the fourth class ammonium ion in formula (I).

[Claim 5] The refining method according to claim 4 which is a tetra alkylammonium cation in which the fourth class ammonium ion is shown by following general formula (II).

[Formula 2]  $NR^1R^2R^3R^4+$  (II)

( $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  express the alkyl group of the carbon numbers 1-3 independently among a formula, respectively.)  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  may be combined mutually.

[Claim 6] The refining method according to claim 1 or 2 whose  $Q^+$  is a lithium ion in formula (I).

[Claim 7] Alcohol is methanol, ethanol, n-propanol, or isopropanol, Halogenated alkane is chloroform, dichloromethane, 1,1-dichloroethane, or 1,2-dichloroethane, And the refining method according to claim 2 whose chain carboxylate is methyl acetate, ethyl acetate, acetic acid-n-propyl, acetic acid-n-butyl, methyl propionate, or ethyl propionate.

[Claim 8] An electrochemical capacitor or a lithium cell using a salt obtained from an anode, a negative electrode, and a nonaqueous electrolyte by one refining method of claims 1 thru/or 7 as a solute of an electrolysis solution in an electrochemical capacitor or a lithium cell constituted at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the refining method of fluoro complex salt. An organic solvent extracts said fluoro complex salt from the mixture containing the fluoro complex salt and impurity of general formula (I) in detail, and it is related with the method of refining.

[0002]

[Formula 3]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

Fluoro complex salt is a useful compound currently used in a wide range of fields as a surface-active agent, the electrolyte for electrochemical elements, and a correlation move catalyst.

[0003]

[Description of the Prior Art] About the manufacturing method of the fluoro complex salt of formula (I), although various methods are known, the method (J. Fluorine Chem., 25, 91 (1984)) to which fluoride salt and neutral inorganic fluoride are made to react like formula (II) in a solvent is usually used.

[0004]

[Formula 4]

$Q^+F + MF_{n-1} \rightarrow Q^+MF_n^-$  (II)

(The inside of a formula,  $Q^+$ , and M are synonymous with formula (I))

However, the obtained salt reacts to a raw material, a solvent, and the water mixed in very small quantities from the air middle class, [0005]

[Formula 5]

$Q^+MF_n^- + XH_2O \rightleftharpoons Q^+MF_{n-x}(OH)_x + XHF$  (III)

[0006] ( $Q^+$  and M are synonymous with formula (I) among a formula, and X is an integer of 1 - n)

Since hydrolysis like formula (III) is caused, in the generated  $Q^+MF_n^-$  salt, hydrolysis product  $Q^+MF_{n-x}(OH)_x^-$  (x= 1, 2, ..., n) and  $Q^+F^-$  will be contained as an impurity.  $MF_{n-1}$  of a raw material also reacts to water or various organic matters easily, for example,  $MF_{(n-1)-x}(OH)_x$  (x= 1, 2, ..., n-1) generates by a reaction with moisture.

[0007] In order to avoid hydrolysis, it may react by using anhydrous hydrogen fluoride as a solvent, but hydrogen fluoride sticks to a generation salt and there is a problem that desorption is difficult. For this reason, in order to obtain the fluoro complex salt of a high grade from the mixture (it may be hereafter called rough fluoro complex salt or crude salt) containing the fluoro complex salt and impurity which were obtained, for example by the reaction of formula (II), refining by the recrystallization of a crude material is usually performed.

[0008]

[Problem(s) to be Solved by the Invention] However, about the recrystallization of crude salt, a long time is required, and moreover, there are also many losses of output and they have the problem of not being economical. This invention tends to provide the method of obtaining the fluoro complex salt of a high grade with high yield by simple operation.

[0009]

[Means for Solving the Problem] A result of having considered wholeheartedly extraction by a solvent of fluoro complex salt which this invention persons make the purpose from a crude salt solid in view of this situation, When

a specific solvent is used, only fluoro complex salt is eluted in a solvent, and it finds out that fluoro complex salt of a high grade is obtained by simple operation of a \*\* exception and solvent distilling off, and came to complete this invention.

[0010] That is, there is a gist of this invention, without a refining method of fluoro complex salt extracting said fluoro complex salt from a mixture containing fluoro complex salt and impurity which are shown by following general formula (I) using an organic solvent which dissolves said fluoro complex salt and does not dissolve said impurity.

[0011]

[Formula 6]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

[0012]

[Embodiment of the Invention] This invention extracts said fluoro complex salt from the mixture containing specific fluoro complex salt and impurity using an organic solvent. The hydrolysis product of the fluoro complex salt used as impurity, for example with the purpose here, the hydrolysis product of  $Q^+MF_{n-x}(OH)_x^-$  ( $x=1, 2, \dots, n$ ) or a raw material,  $MF_{(n-1)-x}(OH)_x$  ( $x=1, 2, \dots, n-1$ ) etc. are pointed out.

[0013] The fluoro complex salt which is the target of this invention is shown by formula (I).

[0014]

[Formula 7]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

In formula (I), when  $Q^+$  is a metal ion, limitation in particular is not carried out about a metal ion, but alkali metal ion is preferred and a lithium ion is preferred in alkali metal ion.

[0015] When  $Q^+$  is organic onium ion, it is not limited in particular for organic onium ion, but the fourth class onium ion is preferred, and the fourth class ammonium ion is preferred in the fourth class onium ion. Various kinds of tetra alkyl ammonium as an example of the fourth class ammonium ion for example, For example, various pyrrolidinium, such as N,N-dimethylpyrrolidinium and N-ethyl-N-ethyl pyrrolidinium, For example, N,N'-dimethyl imidazolinium, N-ethyl-N'-methyl imidazolinium, 1, 2, 3-trimethyl imidazolinium, 1 and 3, 4-trimethyl imidazolinium, 1-ethyl-2,3-dimethyl imidazolinium, 1-ethyl-3,4-dimethyl imidazolinium, 2-ethyl-1,3-dimethyl imidazolinium, 4-ethyl-2,3-dimethyl imidazolinium, 1,2-diethyl-3-methyl imidazolinium, 1,3-diethyl-2-methyl imidazolinium, 1,3-diethyl-4-methyl imidazolinium, 1,2-diethyl-3-methyl imidazolinium, 1,4-diethyl-3-methyl imidazolinium, 1 and 2, 3-triethyl imidazolinium, 1,3,4-triethyl imidazolinium, 1,2,3,4-tetramethyl imidazolinium, 1-ethyl-2,3,4-trimethyl imidazolinium, the 1-ethyl-2 and 3, 5-trimethyl imidazolinium, 1-ethyl-3,4,5-trimethyl imidazolinium, the 2-ethyl-1 and 3, 4-trimethyl imidazolinium, 4-ethyl-1,2,3-trimethyl imidazolinium, the 4-ethyl-1 and 3, 5-trimethyl imidazolinium, 1,2-diethyl-3,4-dimethyl imidazolinium, 1,2-diethyl-3,5-dimethyl imidazolinium, 1,3-diethyl-2,4-dimethyl imidazolinium, 1,3-diethyl-2,5-dimethyl imidazolinium, 1,4-diethyl-2,3-dimethyl imidazolinium, 1,5-diethyl-2,3-dimethyl imidazolinium, 1,5-diethyl-3,4-dimethyl imidazolinium, 2,3-diethyl-1,4-dimethyl imidazolinium, 2,3-diethyl-1,5-dimethyl imidazolinium, 2,4-diethyl-1,5-dimethyl imidazolinium, 2,5-diethyl-1,3-dimethyl imidazolinium, 3,4-diethyl-1,2-dimethyl imidazolinium, 3,4-diethyl-1,5-dimethyl imidazolinium, 3,5-diethyl-1,2-dimethyl imidazolinium, 3,5-diethyl-1,4-dimethyl imidazolinium, 4,5-diethyl-1,3-dimethyl imidazolinium, 1,2,3-triethyl 4-methyl imidazolinium, 1,3,4-triethyl 2-methyl imidazolinium, 1,3,4-triethyl 5-methyl imidazolinium, 2,3,4-triethyl 1-methyl imidazolinium, 2,3,5-triethyl 1-methyl imidazolinium, 3,4,5-triethyl 1-methyl imidazolinium, 1, 2 and 3, 4-tetraethyl imidazolinium, Various imidazolinium, such as 1, 3, 4, and 5-tetraethyl imidazolinium, For example, N,N'-dimethyl tetrahydro pilus MIJINIUMU, N-ethyl-N-methyl tetrahydro pilus MIJINIUMU, 1,2,3-trimethyl tetrahydro pilus MIJINIUMU, N,N'-diethyl tetrahydro pilus MIJINIUMU, N-methyl diazabicyclo NONENIUMU, N-ethyl diazabicyclo NONENIUMU, Various tetrahydro pilus midge NIUMU, for example, N,N-dimethyl mol HORINIUMU, such as N-methyl diazabicyclo UNDESENIUMU and N-ethyl diazabicyclo UNDESENIUMU, N-ethyl-N-methyl mol HORINIUMU, N,N-diethyl mol HORINIUMU, etc., Various mol HORINIUMU compounds, for example, N,N-dimethyl PIPERAJINIUMU, Various alicyclic ammonium ion, such as various PIPERAJINIUMU, such as N-ethyl-N-methyl PIPERAJINIUMU and N,N-diethyl PIPERAJINIUMU, For example, various pyridinium, such as N-methylpyridinium and N-ethylpyridinium, For example, N,N'-dimethyl imidazolinium, N-ethyl-N-methyl imidazolinium, 1, 2, 3-trimethyl imidazolinium, 1 and 3, 4-trimethyl imidazolinium, 1-ethyl-2,3-dimethyl imidazolinium, 1-ethyl-3,4-dimethyl imidazolinium, 2-ethyl-1,3-dimethyl imidazolinium, 4-ethyl-2,3-

dimethyl imidazolium, 1,2-diethyl- 3-methyl imidazolium, 1,3-diethyl- 2-methyl imidazolium, 1,3-diethyl- 4-methyl imidazolium, 1,2-diethyl- 3-methyl imidazolium, 1,4-diethyl- 3-methyl imidazolium, 1 and 2, 3-triethyl imidazolium, 1 and 3, 4-triethyl imidazolium, 1, 2 and 3, 4-tetramethyl imidazolium, 1-ethyl-2,3,4-trimethyl imidazolium, the 1-ethyl- 2 and 3, 5-trimethyl imidazolium, 1-ethyl-3,4,5-trimethyl imidazolium, the 2-ethyl- 1 and 3, 4-trimethyl imidazolium, 4-ethyl-1,2,3-trimethyl imidazolium, the 4-ethyl- 1 and 3, 5-trimethyl imidazolium, 1,2-diethyl- 3,4-dimethyl imidazolium, 1,2-diethyl- 3,5-dimethyl imidazolium, 1,3-diethyl- 2,4-dimethyl imidazolium, 1,3-diethyl- 2,5-dimethyl imidazolium, 1,4-diethyl- 2,3-dimethyl imidazolium, 1,5-diethyl- 2,3-dimethyl imidazolium, 1,5-diethyl- 3,4-dimethyl imidazolium, 2,3-diethyl- 1,4-dimethyl imidazolium, 2,3-diethyl- 1,5-dimethyl imidazolium, 2,4-diethyl- 1,5-dimethyl imidazolium, 2,5-diethyl- 1,3-dimethyl imidazolium, 3,4-diethyl- 1,2-dimethyl imidazolium, 3,4-diethyl- 1,5-dimethyl imidazolium, 3,5-diethyl- 1,2-dimethyl imidazolium, 3,5-diethyl- 1,4-dimethyl imidazolium, 4,5-diethyl- 1,3-dimethyl imidazolium, 1,2,3-triethyl 4-methyl imidazolium, 1,3,4-triethyl 2-methyl imidazolium, 1,3,4-triethyl 5-methyl imidazolium, 2,3,4-triethyl 1-methyl imidazolium, 2,3,5-triethyl 1-methyl imidazolium, Although various aromatic ammonium ion, such as various imidazolium, such as 3,4,5-triethyl 1-methyl imidazolium, 1,2,3,4-tetraethyl imidazolium, and 1,3,4,5-tetraethyl imidazolium, is mentioned, The tetra alkylammonium ion expressed with formula (II) also in it is still more preferred.

[0016]

[Formula 8]  $\text{NR}^1\text{R}^2\text{R}^3\text{R}^4+$  (II)

( $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  express the alkyl group of the carbon numbers 1-3 independently among a formula, respectively.)  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  may be combined mutually.

in formula (II) — the carbon number of an alkyl group — 1-3 — it is 1-2 preferably. And as for the sum total of the carbon number of an alkyl group, it is preferred that it is 4-8. As an example of an alkyl group, are a methyl group, an ethyl group, and a propyl group, and as an example of such tetra alkylammonium. For example, tetraethylammonium, triethyl methylammonium, Diethyl dimethylammonium, ethyl trimethylammonium, tetramethylammonium, dimethylpyrrolidinium, ethylmethyl pyrrolidinium, diethyl pyrrolidinium, dimethyl piperidinium, ethylmethyl piperidinium, etc. are mentioned. These are independent, or can be combined and used.

[0017]As an example of  $\text{M}$  of  $\text{MF}_n^-$ , Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, nickel, Cu, B, aluminum, Si, germanium, P, As, Sb, S, Se, Te, Cl, Br, and I are mentioned, for example. Ti, Zr, V, Nb, Ta, B, aluminum, Si, P, etc. are preferred in these. As an example of  $\text{MF}_n^-$ , for example  $\text{TiF}_6^-$ ,  $\text{ZrF}_6^-$ ,  $\text{ZrF}_5^-$ ,  $\text{ZrF}_4^-$ ,  $\text{VF}_6^-$ ,  $\text{VF}_5^-$ ,  $\text{VF}_4^-$ ,  $\text{VF}_3^-$ ,  $\text{NbF}_6^-$ ,  $\text{NbF}_5^-$ ,  $\text{TaF}_6^-$ ,  $\text{MoF}_7^-$ ,  $\text{WF}_6^-$ ,  $\text{MnF}_7^-$ ,  $\text{FeF}_3^-$ ,  $\text{CoF}_3^-$ ,  $\text{NiF}_3^-$ ,  $\text{CuF}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{AlF}_4^-$ ,  $\text{SiF}_5^-$ ,  $\text{GeF}_5^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{SF}_7^-$ ,  $\text{SeF}_7^-$ ,  $\text{TeF}_5^-$ ,  $\text{ClF}_6^-$ ,  $\text{BrF}_6^-$ ,  $\text{IF}_6^-$ , etc. are mentioned.  $\text{TiF}_5^-$ ,  $\text{ZrF}_5^-$ ,  $\text{VF}_6^-$ ,  $\text{NbF}_6^-$ ,  $\text{TaF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{AlF}_4^-$ ,  $\text{SiF}_5^-$ ,  $\text{PF}_6^-$ , etc. are preferred in these. These are independent, or can be combined and used.

[0018]Although it is not limited and various kinds of methods can be used especially about a manufacturing method of rough fluoro complex salt, Since a raw material and an objective product have very strong hygroscopicity, in order to avoid moisture absorption as much as possible and to suppress generation of impurities, such as hydrolyzate, as much as possible in the manufacture, it is [ 0 \*\* or less of dew point ] preferred to operate it under atmosphere -30 \*\* or less still more preferably.

[0019]About extraction by this invention method, a predetermined organic solvent is added to crude salt obtained in this way, and it is preferably carried out under churning. About an obtained extract, fluoro complex salt of a high grade made into the purpose is obtained by removing a solvent from the filtrate after filtration. It must be a solvent which only an object dissolves and an impurity does not dissolve as a solvent used for extraction. It is considered as such a solvent and alcohol, halogenated alkane, acetonitrile, and a chain carboxylate solvent are preferred. Alcohol specifically methanol, ethanol, n-propanol, isopropanol, and halogenated alkane, Chloroform, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, Chain carboxylate Methyl acetate, ethyl acetate, butyl acetate, amyl acetate, Methyl propionate, ethyl propionate, propionic acid-n-propyl, propionic acid isopropyl, propionic acid-n-butyl, propionic acid isobutyl, propionic acid-t-butyl, etc. are mentioned.

[0020]Acetonitrile, isopropanol, dichloromethane, 1,2-dichloroethane, and ethyl acetate are preferred in these.

These are independent, or can be used together two or more sorts, and can be used. As for the amount of solvents used for extraction, it is preferred to use 1-50 times the amount by weight to crude salt, and it is still more preferred to use 2-10 times the amount.

[0021]300 ppm or less of water content in an extracting solvent is 100 ppm or less preferably. Since an impurity dissolves in water and purity falls, it is not desirable, except that a hydrolysis reaction of a salt will occur and a yield of a salt will fall, if water content exceeds 300 ppm. As for temperature at the time of extraction, -20-100 \*\* is preferred, and it is still more preferred. [ of 20-60 \*\* ] If too low, a dissolved amount to a solvent will become

less, and if too high, decomposition and evaporation of a solvent will take place.

[0022] Since evaporation of a solvent will take place if too long [ if too short, it will become insufficient, and ], extraction time of less than 24 hours is preferred 30 minutes or more, and is still more preferred for 1 hour or more. [ of less than 10 hours ] Although filtration may use which methods, such as ordinary pressure, decompression, application of pressure, and centrifugality, it needs to take care so that a solvent may not volatilize so much during work. In order to avoid hydrolysis under filtration work, it is necessary to keep still more desirable preferably 0 \*\* or less of dew point of atmosphere when a filtration apparatus is installed at -30 \*\* or less.

[0023] After filtration, although it changes with the boiling point of a solvent in which a solvent from filtrate was distilled off in order to obtain an object, but a minimum used temperature at the time of distilling off, and pressures at the time of distilling off, that an extract is independent or in order to avoid thermal reaction between solvents, a maximum of 100 \*\* or less is preferred, and is still more preferred. [ of 60 \*\* or less ] As for a pressure, it is preferred to carry out by decompression in order to avoid a rise of temperature. Use as a solute of nonaqueous electrolyte used for electrochemical devices, such as an electrochemical capacitor or a lithium cell, is possible for a salt obtained by a refining method of this invention.

[0024]

[Example] Although an example is given to below and this invention is explained to it still in detail, this invention is not limited to these examples, unless the gist is exceeded.

Composition of example 1 operation 1 crude hexafluoride tantalate triethyl methylammonium; the reaction agent which carried out dry drying altogether here was used. For example, acetonitrile of the solvent used that whose moisture content is 30 ppm.

[0025] In the 300-cc flask made from PFA replaced with dew point-70 \*\* nitrogen, the agitation mix of 13.8 g (1.02 mol) of the triethyl fluoridation methylammonium was carried out for acetonitrile to 50 ml at 25 \*\*, and suspension was obtained. When 27.6 g (1.00 mol) of tantalum pentafluoride was gradually added to this, it agitated at 25 \*\* after the end of addition for further 1 hour and filtration removed the insoluble matter of tantalum pentafluoride origin, the water-white solution was obtained.

[0026] 40.0g of crude hexafluoride tantalate triethyl methylammonium was obtained by carrying out decompression distilling off of the acetonitrile at 25 \*\* from this solution, and also heating and carrying out reduced pressure drying to 40 \*\* for 2 hours. In order to conduct <sup>19</sup>F-NMR analysis of this crude thing, when heavy DMSO which is a measurement solvent was added to crude things, insoluble precipitate arose. When analyzed using supernatant liquid, the peak of TaF<sub>6</sub><sup>-</sup> origin was observed near delta 40 ppm (CFCl<sub>3</sub> standard), and also it is delta -100 ppm

(CFCl<sub>3</sub>). The peak of F<sup>-</sup> origin was observed near the <sub>3</sub> standard, and also some unknown peaks were accepted.

[0027] The operation 2 refining of crude hexafluoride tantalate triethyl methylammonium; 100 ml of 1,2-dichloroethane was added to crude hexafluoride tantalate triethyl methylammonium, and it agitated at the room temperature for 2 hours. Under the present circumstances, since the impurity of the tantalum pentafluoride origin included in crude things did not dissolve in 1,2-dichloroethane, the solution containing a little white sediments was obtained. After removing this sediment according to \*\* under a nitrogen atmosphere, decompression distilling off of the 1,2-dichloroethane was carried out at 25 \*\*, and the white solid was obtained. By heating and carrying out reduced pressure drying of this to 40 more \*\* for 2 hours, 32.9g of hexafluoride tantalate triethyl methylammonium of the high grade was obtained. Yield was 80%. the place which carried out <sup>19</sup>F-NMR analysis — delta 40 ppm (a CFCl<sub>3</sub> standard.) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the singlet originating in hexafluoride tantalate ion to the DMSO-d<sub>6</sub> solvent, but it checked that it was

hexafluoride tantalate triethyl methylammonium of a high grade.

[0028] In order to investigate the characteristic as a solute of the electrolysis solution for operation 3 electrochemical capacitors, hexafluoride tantalate triethyl methylammonium was dissolved in propylene carbonate so that it might become in 1. and 1.0 mol /, and nonaqueous electrolyte was prepared. Using this nonaqueous electrolyte, glassy carbon was used for the working pole, it was considered as the measurement temperature of 25 \*\*, and the sweep rate of 5mV/second, and polarization measurement was performed using the Ag/Ag<sup>+</sup> electrode standard to potential in case the current of absolute value 1 mA/cm<sup>2</sup> flows from 0V, respectively in an oxidation side and reduction side.

[0029] The potential of the oxidation side 3.3V into which the current of absolute value 1 mA/cm<sup>2</sup> flowed is reduction side -3.7V, and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of 1 mA/cm<sup>2</sup> flowed through the oxidation and reduction side

from 0V. A result is shown in Table 1.

Except having used 18.8 g (1.00 mol) of niobium pentafluoride instead of example 2 tantalum pentafluoride, when reaction and refining were performed on the same conditions as Example 1, 25.9g of hexafluoride niobate triethyl methylammonium of the high grade was obtained. Yield was 80%.

[0030]When  $^{19}\text{F}$ -NMR analysis is carried out, to  $\delta 100\text{ppm}$ . (A  $\text{CFCl}_3$  standard, a  $\text{DMSO}-d_6$  solvent) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the 10-fold line ( $J=\text{Hz}$ ) originating in hexafluoride niobate ion, but it checked that it was hexafluoride niobate triethyl methylammonium of a high grade. When polarization measurement is performed on the same conditions as the operation 3 of Example 1, the current of absolute value  $1\text{ mA/cm}^2$  the potential which flowed The oxidation side  $3.3\text{V}$ . It is reduction side  $-3.7\text{V}$  and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of  $0\text{V}$  to  $1\text{ mA/cm}^2$  flowed through the oxidation and reduction side.

[0031]the place which performed reaction and refining on the same conditions as Example 1 except having used  $2.6\text{ g}$  ( $1.02\text{ mol}$ ) of lithium fluoride instead of example 3 fluoridation [ triethyl ] methylammonium — the lithium tantalate hexafluoride  $15.0\text{g}$  of a high grade — it obtained. Yield was 70%.

[0032]the place which carried out  $^{19}\text{F}$ -NMR analysis —  $\delta 40\text{ppm}$  (a  $\text{CFCl}_3$  standard.) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the singlet originating in hexafluoride tantalate ion to the  $\text{DMSO}-d_6$  solvent, but it checked that it was lithium tantalate hexafluoride of a high grade.

When polarization measurement is performed on the same conditions as the operation 3 of Example 1, the current of absolute value  $1\text{ mA/cm}^2$  the potential which flowed The oxidation side  $3.3\text{V}$ , It is reduction side  $-4.0\text{V}$  and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of  $0\text{V}$  to  $1\text{ mA/cm}^2$  flowed through the oxidation and reduction side.

[0033]As opposed to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of four to example 8 Example 1, The extracting solvent used for refining operation of the operation 2, respectively Dichloromethane, Except having changed into ethyl acetate, acetonitrile, methanol, and 1,2-dichloroethane, on the same conditions as operation of Example 1, respectively, When reaction and refining operation were performed and  $^{19}\text{F}$ -NMR analysis was conducted, also in which example, the signal of impurity origin was not accepted at all, but it checked that it was hexafluoride tantalate triethyl methylammonium of a high grade. In the place which performed polarization measurement of the operation 3, and which example, the current originating in the electrochemical reaction of an impurity was not able to be checked.

[0034]A result is shown in Table 1.

Although the acetone  $50\text{g}$  was added and heating and dissolving were tried to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of comparative example 1 Example 1, the whole quantity was not dissolved but some white solids remained.

[0035]Although  $100\text{ g}$  was added and heating and dissolving were tried, the whole quantity did not dissolve.  $8.2\text{ g}$  was obtained when the \*\* exception carried out the crystal obtained by cooling filtrate and performing recrystallization, after adding the acetone  $50\text{g}$ , heating again to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of Example 1 and hot filtration's removing a sediment under a nitrogen atmosphere. Yield was 20%. The peak which the chemical shift of the singlet originating in hexafluoride tantalate ion was checked when  $^{19}\text{F}$ -NMR analysis was carried out, and also is considered to be fluoride ion near  $\delta -100\text{ ppm}$  was checked, and also many unknown peaks were checked, and it checked that it was low purity.

[0036]When polarization measurement was performed on the same conditions as the operation 3 of Example 1, many peaks of impurity origin were detected.

It compounded on the same conditions as Example 1 except having changed into n-hexane the extracting solvent used for refining operation of the operation 2 from 1,2-dichloroethane to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of comparative example 2 Example 1. Although the agitation mix of crude hexafluoride tantalate triethyl methylammonium and n-hexane was carried out, even if it existed while it had been insoluble in most and distilled off the extract layer of the back according to \*\*, hexafluoride tantalate triethyl methylammonium was not obtained at all. The result was the same, even if the quantity of n-hexane was increased to  $500\text{ ml}$  and it performed same operation.

[0037]Although reaction and refining operation were performed on the same conditions as the comparative example 1, respectively except having changed into comparative example 3 extracting solvent from n-hexane at toluene, even if it distilled off the extract layer of the back according to \*\*, hexafluoride tantalate triethyl methylammonium was not obtained at all.

表 1

	QMF-塩	抽出溶媒	収率	<sup>1</sup> H-NMR分析結果	分電測定結果
実施例 1	六フッ化タンタル酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	80%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 2	六フッ化エーオプ酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	75%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 3	六フッ化タンタル酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	70%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 4	六フッ化タンタル酸トリエチルメチルアンモニウム	ジクロロエタン	70%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 5	六フッ化タンタル酸トリエチルメチルアンモニウム	酢酸エチル	65%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 6	六フッ化タンタル酸トリエチルメチルアンモニウム	アセトニトリル	65%	目的物のピークのみ検出	不純物ピーク検出せず
実施例 7	六フッ化タンタル酸トリエチルメチルアンモニウム	メタノール	60%	目的物のピークのみ検出	不純物ピーク検出せず
比較例 1	六フッ化タンタル酸トリエチルメチルアンモニウム	アセトン	20%	ピークを多数検出	不純物ピークを多数検出
比較例 2	六フッ化タンタル酸トリエチルメチルアンモニウム	n-ヘキサン	0%		
比較例 3	六フッ化タンタル酸トリエチルメチルアンモニウム	トルエン	0%		

[0039]  
[Effect of the Invention] According to this invention, the fluoro complex salt of a high grade can be obtained with high yield by simple operation.



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TECHNICAL FIELD

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[Field of the Invention]This invention relates to the refining method of fluoro complex salt. An organic solvent extracts said fluoro complex salt from the mixture containing the fluoro complex salt and impurity of general formula (I) in detail, and it is related with the method of refining.

[0002]

[Formula 3] $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

Fluoro complex salt is a useful compound currently used in a wide range of fields as a surface-active agent, the electrolyte for electrochemical elements, and a correlation move catalyst.

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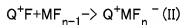
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PRIOR ART

[Description of the Prior Art]About the manufacturing method of the fluoro complex salt of formula (I), although various methods are known, the method (J. Fluorine Chem., 25, 91 (1984)) to which fluoride salt and neutral inorganic fluoride are made to react like formula (II) in a solvent is usually used.

[0004]

[Formula 4]



(The inside of a formula,  $Q^+$ , and M are synonymous with formula (I))

However, the obtained salt reacts to a raw material, a solvent, and the water mixed in very small quantities from the air middle class,[0005]

[Formula 5]



[0006]( $Q^+$  and M are synonymous with formula (I) among a formula, and X is an integer of  $1 - n$ )

Since hydrolysis like formula (III) is caused, in the generated  $Q^+MF_n^-$  salt, hydrolysis product  $Q^+MF_{n-x}(OH)_x^-$  ( $x = 1, 2, \dots, n$ ) and  $Q^+F^-$  will be contained as an impurity.  $MF_{n-1}$  of a raw material also reacts to water or various organic matters easily, for example,  $MF_{(n-1)-[x]}(OH)_x$  ( $x = 1, 2, \dots, n-1$ ) generates by a reaction with moisture.

[0007]In order to avoid hydrolysis, it may react by using anhydrous hydrogen fluoride as a solvent, but hydrogen fluoride sticks to a generation salt and there is a problem that desorption is difficult. For this reason, in order to obtain fluoro complex salt of a high grade from a mixture (it may be hereafter called rough fluoro complex salt or crude salt) containing fluoro complex salt and impurity which were obtained, for example by the reaction of formula (II), refining by recrystallization of a crude material is usually performed.

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**EFFECT OF THE INVENTION**

---

[Effect of the Invention]According to this invention, the fluoro complex salt of a high grade can be obtained with high yield by simple operation.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention]However, about the recrystallization of crude salt, a long time is required, and moreover, there are also many losses of output and they have the problem of not being economical. This invention tends to provide the method of obtaining the fluoro complex salt of a high grade with high yield by simple operation.

[0009]

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## MEANS

[Means for Solving the Problem] A result of having considered wholeheartedly extraction by a solvent of fluoro complex salt which this invention persons make the purpose from a crude salt solid in view of this situation, When a specific solvent is used, only fluoro complex salt is eluted in a solvent, and it finds out that fluoro complex salt of a high grade is obtained by simple operation of a \*\* exception and solvent distilling off, and came to complete this invention.

[0010] That is, there is a gist of this invention, without a refining method of fluoro complex salt extracting said fluoro complex salt from a mixture containing fluoro complex salt and impurity which are shown by following general formula (I) using an organic solvent which dissolves said fluoro complex salt and does not dissolve said impurity.

[0011]

[Formula 6]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

[0012]

[Embodiment of the Invention] This invention extracts said fluoro complex salt from the mixture containing specific fluoro complex salt and impurity using an organic solvent. The hydrolysis product of the fluoro complex salt used as impurity, for example with the purpose here, the hydrolysis product of  $Q^+MF_{n-x}(OH)_x^-$  ( $x=1, 2, \dots, n$ ) or a raw material,  $MF_{(n-1)-x}(OH)_x$  ( $x=1, 2, \dots, n-1$ ) etc. are pointed out.

[0013] The fluoro complex salt which is the target of this invention is shown by formula (I).

[0014]

[Formula 7]  $Q^+MF_n^-$  (I)

( $Q^+$  expresses organic onium ion or a metal ion among a formula, M expresses four to periodic table 16 fellows' element, and n expresses the integer of 3-7)

In formula (I), when  $Q^+$  is a metal ion, limitation in particular is not carried out about a metal ion, but alkali metal ion is preferred and a lithium ion is preferred in alkali metal ion.

[0015] When  $Q^+$  is organic onium ion, it is not limited in particular for organic onium ion, but the fourth class onium ion is preferred, and the fourth class ammonium ion is preferred in the fourth class onium ion. Various kinds of tetra alkylammonium as an example of the fourth class ammonium ion for example, For example, various pyrrolidinium, such as N,N-dimethylpyrrolidinium and N-ethyl-N-ethyl pyrrolidinium, For example, N,N'-dimethyl imidazolinium, N-ethyl-N'-methyl imidazolinium, 1, 2, 3-trimethyl imidazolinium, 1 and 3, 4-trimethyl imidazolinium, 1-ethyl-2,3-dimethyl imidazolinium, 1-ethyl-3,4-dimethyl imidazolinium, 2-ethyl-1,3-dimethyl imidazolinium, 4-ethyl-2,3-dimethyl imidazolinium, 1,2-diethyl- 3-methyl imidazolinium, 1,3-diethyl- 2-methyl imidazolinium, 1,3-diethyl- 4-methyl imidazolinium, 1,2-diethyl- 3-methyl imidazolinium, 1,4-diethyl- 3-methyl imidazolinium, 1 and 2, 3-triethyl imidazolinium, 1,3,4-triethyl imidazolinium, 1,2,3,4-tetramethyl imidazolinium, 1-ethyl-2,3,4-trimethyl imidazolinium, the 1-ethyl- 2 and 3, 5-trimethyl imidazolinium, 1-ethyl-3,4,5-trimethyl imidazolinium, the 2-ethyl- 1 and 3, 4-trimethyl imidazolinium, 4-ethyl-1,2,3-trimethyl imidazolinium, the 4-ethyl- 1 and 3, 5-trimethyl imidazolinium, 1,2-diethyl- 3,4-dimethyl imidazolinium, 1,2-diethyl- 3,5-dimethyl imidazolinium, 1,3-diethyl- 2,4-dimethyl imidazolinium, 1,3-diethyl- 2,5-dimethyl imidazolinium, 1,4-diethyl- 2,3-dimethyl imidazolinium, 1,5-diethyl- 2,3-dimethyl imidazolinium, 1,5-diethyl- 3,4-dimethyl imidazolinium, 2,3-diethyl- 1,4-dimethyl imidazolinium, 2,3-diethyl- 1,5-dimethyl imidazolinium, 2,4-diethyl- 1,5-dimethyl imidazolinium, 2,5-diethyl- 1,3-dimethyl imidazolinium, 3,4-diethyl- 1,2-dimethyl imidazolinium, 3,4-diethyl- 1,5-dimethyl imidazolinium, 3,5-diethyl- 1,2-dimethyl imidazolinium, 3,5-diethyl- 1,4-dimethyl imidazolinium, 4,5-diethyl- 1,3-dimethyl

imidazolinium, 1,2,3-triethyl 4-methyl imidazolinium, 1,3,4-triethyl 2-methyl imidazolinium, 1,3,4-triethyl 5-methyl imidazolinium, 2,3,4-triethyl 1-methyl imidazolinium, 2,3,5-triethyl 1-methyl imidazolinium, 3,4,5-triethyl 1-methyl imidazolinium, 1, 2 and 3, 4-tetraethyl imidazolinium, Various imidazolinium, such as 1, 3, 4, and 5-tetraethyl imidazolinium, For example, N,N'-dimethyl tetrahydro pilus MIJINIUMU, N-ethyl-N-methyl tetrahydro pilus MIJINIUMU, 1,2,3-trimethyl tetrahydro pilus MIJINIUMU, N,N'-diethyl tetrahydro pilus MIJINIUMU, N-methyl diazabicyclo NONENIUMU, N-ethyl diazabicyclo NONENIUMU, Various tetrahydro pilus midge NIUMU, for example, N,N-dimethyl mol HORINIUMU, such as N-methyl diazabicyclo UNDESENIUMU and N-ethyl diazabicyclo UNDESENIUMU, N-ethyl-N-methyl mol HORINIUMU, N,N-diethyl mol HORINIUMU, etc., Various mol HORINIUMU compounds, for example, N,N-dimethyl PIPERAJINIUMU, Various alicyclic ammonium ion, such as various PIPERAJINIUMU, such as N-ethyl-N-methyl PIPERAJINIUMU and N,N-diethyl PIPERAJINIUMU. For example, various pyridinium, such as N-methylpyridinium and N-ethylpyridinium, For example, N,N'-dimethyl imidazolinium, N-ethyl-N'-methyl imidazolinium, 1, 2, 3-trimethyl imidazolinium, 1 and 3, 4-trimethyl imidazolinium, 1-ethyl-2,3-dimethyl imidazolinium, 1-ethyl-3,4-dimethyl imidazolinium, 2-ethyl-1,3-dimethyl imidazolinium, 4-ethyl-2,3-dimethyl imidazolinium, 1,2-diethyl-3-methyl imidazolinium, 1,3-diethyl-2-methyl imidazolinium, 1,3-diethyl-4-methyl imidazolinium, 1,2-diethyl-3-methyl imidazolinium, 1,4-diethyl-3-methyl imidazolinium, 1 and 2, 3-triethyl imidazolinium, 1 and 3, 4-triethyl imidazolinium, 1, 2 and 3, 4-tetramethyl imidazolinium, 1-ethyl-2,3,4-trimethyl imidazolinium, the 1-ethyl-2 and 3, 5-trimethyl imidazolinium, 1-ethyl-3,4,5-trimethyl imidazolinium, the 2-ethyl-1 and 3, 4-trimethyl imidazolinium, 4-ethyl-1,2,3-trimethyl imidazolinium, the 4-ethyl-1 and 3, 5-trimethyl imidazolinium, 1,2-diethyl-3,4-dimethyl imidazolinium, 1,2-diethyl-3,5-dimethyl imidazolinium, 1,3-diethyl-2,4-dimethyl imidazolinium, 1,3-diethyl-2,5-dimethyl imidazolinium, 1,4-diethyl-2,3-dimethyl imidazolinium, 1,5-diethyl-2,3-dimethyl imidazolinium, 1,5-diethyl-3,4-dimethyl imidazolinium, 2,3-diethyl-1,4-dimethyl imidazolinium, 2,3-diethyl-1,5-dimethyl imidazolinium, 2,4-diethyl-1,5-dimethyl imidazolinium, 2,5-diethyl-1,3-dimethyl imidazolinium, 3,4-diethyl-1,2-dimethyl imidazolinium, 3,4-diethyl-1,5-dimethyl imidazolinium, 3,5-diethyl-1,2-dimethyl imidazolinium, 3,5-diethyl-1,4-dimethyl imidazolinium, 4,5-diethyl-1,3-dimethyl imidazolinium, 1,2,3-triethyl 4-methyl imidazolinium, 1,3,4-triethyl 2-methyl imidazolinium, 1,3,4-triethyl 5-methyl imidazolinium, 2,3,4-triethyl 1-methyl imidazolinium, 2,3,5-triethyl 1-methyl imidazolinium, Although various aromatic ammonium ion, such as various imidazolinium, such as 3,4,5-triethyl 1-methyl imidazolinium, 1,2,3,4-tetraethyl imidazolinium, and 1,3,4,5-tetraethyl imidazolinium, is mentioned, The tetra alkylammonium ion expressed with formula (II) also in it is still more preferred.

[0016]

[Formula 8]  $\text{NR}^1\text{R}^2\text{R}^3\text{R}^4^{+}(\text{II})$

( $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  express the alkyl group of the carbon numbers 1-3 independently among a formula, respectively.)  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  may be combined mutually.

in formula (II) — the carbon number of an alkyl group — 1-3 — it is 1-2 preferably. And as for the sum total of the carbon number of an alkyl group, it is preferred that it is 4-8. As an example of an alkyl group, are a methyl group, an ethyl group, and a propyl group, and as an example of such tetra alkylammonium, For example, tetraethylammonium, triethyl methylammonium, Diethyl dimethylammonium, ethyl trimethylammonium, tetramethylammonium, dimethylpyrrolidinium, ethylmethyl pyrrolidinium, diethyl pyrrolidinium, dimethyl piperidinium, ethylmethyl piperidinium, etc. are mentioned. These are independent, or can be combined and used.

[0017] As an example of M of  $\text{MF}_n^{+}$ , Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, nickel, Cu, B, aluminum, Si, germanium, P, As, Sb, S, Se, Te, Cl, Br, and I are mentioned, for example, Ti, Zr, V, Nb, Ta, B, aluminum, Si, P, etc. are preferred in these. As an example of  $\text{MF}_n^{+}$ , for example  $\text{TiF}_5$ ,  $\text{ZrF}_4$ ,  $\text{ZrF}_5$ ,  $\text{ZrF}_6$ ,  $\text{VF}_3$ ,  $\text{VF}_4$ ,  $\text{VF}_5$ ,  $\text{VF}_6$ ,  $\text{NbF}_4$ ,  $\text{NbF}_5$ ,  $\text{TaF}_6$ ,  $\text{MoF}_7$ ,  $\text{WF}_6$ ,  $\text{MnF}_7$ ,  $\text{FeF}_3$ ,  $\text{CoF}_3$ ,  $\text{NiF}_3$ ,  $\text{CuF}_3$ ,  $\text{BF}_4$ ,  $\text{AlF}_4$ ,  $\text{SiF}_5$ ,  $\text{GeF}_5$ ,  $\text{PF}_6$ ,  $\text{AsF}_6$ ,  $\text{SbF}_6$ ,  $\text{SF}_7$ ,  $\text{SeF}_7$ ,  $\text{TeF}_5$ ,  $\text{ClF}_6$ ,  $\text{BrF}_6$ ,  $\text{IF}_6$ , etc. are mentioned.  $\text{TiF}_5$ ,  $\text{ZrF}_5$ ,  $\text{VF}_6$ ,  $\text{NbF}_6$ ,  $\text{TaF}_6$ ,  $\text{BF}_4$ ,  $\text{AlF}_4$ ,  $\text{SiF}_5$ ,  $\text{PF}_6$ , etc. are preferred in these. These are independent, or can be combined and used.

[0018] Although it is not limited and various kinds of methods can be used especially about a manufacturing method of rough fluoro complex salt, Since a raw material and an objective product have very strong hygroscopicity, in order to avoid moisture absorption as much as possible and to suppress generation of impurities, such as hydrolyzate, as much as possible in the manufacture, it is [0 \*\* or less of dew point ] preferred to operate it under atmosphere -30 \*\* or less still more preferably.

[0019] About extraction by this invention method, a predetermined organic solvent is added to crude salt obtained in this way, and it is preferably carried out under churning. About an obtained extract, fluoro complex salt of a high grade made into the purpose is obtained by removing a solvent from the filtrate after filtration. It must be a solvent which only an object dissolves and an impurity does not dissolve as a solvent used for extraction. It is

considered as such a solvent and alcohol, halogenated alkane, acetonitrile, and a chain carboxylate solvent are preferred. Alcohol specifically methanol, ethanol, n-propanol, isopropanol, and halogenated alkane, Chloroform, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, Chain carboxylate Methyl acetate, ethyl acetate, butyl acetate, amyl acetate, Methyl propionate, ethyl propionate, propionic acid-n-propyl, propionic acid isopropyl, propionic acid-n-butyl, propionic acid isobutyl, propionic acid-t-butyl, etc. are mentioned.

[0020]Acetonitrile, isopropanol, dichloromethane, 1,2-dichloroethane, and ethyl acetate are preferred in these. These are independent, or can be used together two or more sorts, and can be used. As for the amount of solvents used for extraction, it is preferred to use 1-50 times the amount by weight to crude salt, and it is still more preferred to use 2-10 times the amount.

[0021]300 ppm or less of water content in an extracting solvent is 100 ppm or less preferably. Since an impurity dissolves in water and purity falls, it is not desirable, except that a hydrolysis reaction of a salt will occur and a yield of a salt will fall, if water content exceeds 300 ppm. As for temperature at the time of extraction, -20-100 \*\* is preferred, and it is still more preferred. [ of 20-60 \*\* ] If too low, a dissolved amount to a solvent will become less, and if too high, decomposition and evaporation of a solvent will take place.

[0022]Since evaporation of a solvent will take place if too long [ if too short, it will become insufficient, and ], extraction time of less than 24 hours is preferred 30 minutes or more, and is still more preferred for 1 hour or more. [ of less than 10 hours ] Although filtration may use which methods, such as ordinary pressure, decompression, application of pressure, and centrifugality, it needs to take care so that a solvent may not volatilize so much during work. In order to avoid hydrolysis under filtration work, it is necessary to keep still more desirable preferably 0 \*\* or less of dew point of atmosphere when a filtration apparatus is installed at -30 \*\* or less.

[0023]After filtration, although it changes with the boiling point of a solvent in which a solvent from filtrate was distilled off in order to obtain an object, but a minimum used temperature at the time of distilling off, and pressures at the time of distilling off, that an extract is independent or in order to avoid thermal reaction between solvents, a maximum of 100 \*\* or less is preferred, and is still more preferred. [ of 60 \*\* or less ] As for a pressure, it is preferred to carry out by decompression in order to avoid a rise of temperature. Use as a solute of nonaqueous electrolyte used for electrochemical devices, such as an electrochemical capacitor or a lithium cell, is possible for a salt obtained by a refining method of this invention.

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## EXAMPLE

[Example]Although an example is given to below and this invention is explained to it still in detail, this invention is not limited to these examples, unless the gist is exceeded.

Composition of example 1 operation 1 crude hexafluoride tantalate triethyl methylammonium; the reaction agent which carried out dry drying altogether here was used. For example, acetonitrile of the solvent used that whose moisture content is 30 ppm.

[0025]In the 300-cc flask made from PFA replaced with dew point-70 \*\* nitrogen, the agitation mix of 13.8 g (1.02 mol) of the triethyl fluoridation methylammonium was carried out for acetonitrile to 50 ml at 25 \*\*, and suspension was obtained. When 27.6 g (1.00 mol) of tantalum pentafluoride was gradually added to this, it agitated at 25 \*\* after the end of addition for further 1 hour and filtration removed the insoluble matter of tantalum pentafluoride origin, the water-white solution was obtained.

[0026]40.0g of crude hexafluoride tantalate triethyl methylammonium was obtained by carrying out decompression distilling off of the acetonitrile at 25 \*\* from this solution, and also heating and carrying out reduced pressure drying to 40 \*\* for 2 hours. In order to conduct  $^{19}\text{F}$ -NMR analysis of this crude thing, when heavy DMSO which is a measurement solvent was added to crude things, insoluble precipitate arose. When analyzed using supernatant liquid, the peak of  $\text{TaF}_6^-$  origin was observed near  $\delta 40$  ppm ( $\text{CFCl}_3$  standard), and also it is  $\delta 100$  ppm

( $\text{CFCl}_3$ ). The peak of  $\text{F}^-$  origin was observed near the  $\delta 3$  standard, and also some unknown peaks were accepted.

[0027]The operation 2 refining of crude hexafluoride tantalate triethyl methylammonium; 100 ml of 1,2-dichloroethane was added to crude hexafluoride tantalate triethyl methylammonium, and it agitated at the room temperature for 2 hours. Under the present circumstances, since the impurity of the tantalum pentafluoride origin included in crude things did not dissolve in 1,2-dichloroethane, the solution containing a little white sediments was obtained. After removing this sediment according to \*\* under a nitrogen atmosphere, decompression distilling off of the 1,2-dichloroethane was carried out at 25 \*\*, and the white solid was obtained. By heating and carrying out reduced pressure drying of this to 40 more \*\* for 2 hours, 32.9g of hexafluoride tantalate triethyl methylammonium of the high grade was obtained. Yield was 80%, the place which carried out  $^{19}\text{F}$ -NMR analysis —  $\delta 40$  ppm (a  $\text{CFCl}_3$  standard.) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the singlet originating in hexafluoride tantalate ion to the  $\text{DMSO}-d_6$  solvent, but it checked that it was

hexafluoride tantalate triethyl methylammonium of a high grade.

[0028]In order to investigate the characteristic as a solute of the electrolysis solution for operation 3 electrochemical capacitors, hexafluoride tantalate triethyl methylammonium was dissolved in propylene carbonate so that it might become in 1. and 1.0 mol /, and nonaqueous electrolyte was prepared. Using this nonaqueous electrolyte, glassy carbon was used for the working pole, it was considered as the measurement temperature of 25 \*\*, and the sweep rate of 5mV/second, and polarization measurement was performed using the  $\text{Ag}/\text{Ag}^+$  electrode standard to potential in case the current of absolute value 1  $\text{mA}/\text{cm}^2$  flows from 0V, respectively in an oxidation side and reduction side.

[0029]The potential of the oxidation side 3.3V into which the current of absolute value 1  $\text{mA}/\text{cm}^2$  flowed is reduction side-3.7V, and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of 1  $\text{mA}/\text{cm}^2$  flowed through the oxidation and reduction side from 0V. A result is shown in Table 1.

Except having used 18.8 g (1.00 mol) of niobium pentafluoride instead of example 2 tantalum pentafluoride, when reaction and refining were performed on the same conditions as Example 1, 25.9g of hexafluoride niobate triethyl methylammonium of the high grade was obtained. Yield was 80%.



[0030]When  $^{19}\text{F}$ -NMR analysis is carried out, to  $\delta 100\text{ppm}$ . (A  $\text{CFCl}_3$  standard, a  $\text{DMSO}-d_6$  solvent) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the 10-fold line ( $J=\text{Hz}$ ) originating in hexafluoride tantalate ion, but it checked that it was hexafluoride tantalate triethyl methylammonium of a high grade. When polarization measurement is performed on the same conditions as the operation 3 of Example 1, the current of absolute value  $1\text{ mA/cm}^2$  the potential which flowed The oxidation side  $3.3\text{V}$ , It is reduction side- $3.7\text{V}$  and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of  $0\text{V}$  to  $1\text{ mA/cm}^2$  flowed through the oxidation and reduction side.

[0031]the place which performed reaction and refining on the same conditions as Example 1 except having used  $2.6\text{ g}$  ( $1.02\text{ mol}$ ) of lithium fluoride instead of example 3 fluoridation [ triethyl ] methylammonium — the lithium tantalate hexafluoride  $15.0\text{g}$  of a high grade — it obtained. Yield was  $70\%$ .

[0032]the place which carried out  $^{19}\text{F}$ -NMR analysis —  $\delta 40\text{ppm}$  (a  $\text{CFCl}_3$  standard.) The signal of impurity origin was not accepted at all other than having checked the chemical shift of the singlet originating in hexafluoride tantalate ion to the  $\text{DMSO}-d_6$  solvent, but it checked that it was lithium tantalate hexafluoride of a high grade.

When polarization measurement is performed on the same conditions as the operation 3 of Example 1, the current of absolute value  $1\text{ mA/cm}^2$  the potential which flowed The oxidation side  $3.3\text{V}$ , It is reduction side- $4.0\text{V}$  and the current originating in the electrochemical reaction of an impurity was not able to be checked before the potential into which the current of  $0\text{V}$  to  $1\text{ mA/cm}^2$  flowed through the oxidation and reduction side.

[0033]As opposed to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of four to example 8 Example 1, The extracting solvent used for refining operation of the operation 2, respectively Dichloromethane, Except having changed into ethyl acetate, acetonitrile, methanol, and 1,2-dichloroethane, on the same conditions as operation of Example 1, respectively, When reaction and refining operation were performed and  $^{19}\text{F}$ -NMR analysis was conducted, also in which example, the signal of impurity origin was not accepted at all, but it checked that it was hexafluoride tantalate triethyl methylammonium of a high grade. In the place which performed polarization measurement of the operation 3, and which example, the current originating in the electrochemical reaction of an impurity was not able to be checked.

[0034]A result is shown in Table 1.

Although the acetone  $50\text{g}$  was added and heating and dissolving were tried to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of comparative example 1 Example 1, the whole quantity was not dissolved but some white solids remained.

[0035]Although  $100\text{ g}$  was added and heating and dissolving were tried, the whole quantity did not dissolve.  $8.2\text{ g}$  was obtained when the \*\* exception carried out the crystal obtained by cooling filtrate and performing recrystallization, after adding the acetone  $50\text{g}$ , heating again to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of Example 1 and hot filtration's removing a sediment under a nitrogen atmosphere. Yield was  $20\%$ . The peak which the chemical shift of the singlet originating in hexafluoride tantalate ion was checked when  $^{19}\text{F}$ -NMR analysis was carried out, and also is considered to be fluoride ion near  $\delta 100\text{ ppm}$  was checked, and also many unknown peaks were checked, and it checked that it was low purity.

[0036]When polarization measurement was performed on the same conditions as the operation 3 of Example 1, many peaks of impurity origin were detected.

It compounded on the same conditions as Example 1 except having changed into n-hexane the extracting solvent used for refining operation of the operation 2 from 1,2-dichloroethane to the crude hexafluoride tantalate triethyl methylammonium obtained by the operation 1 of comparative example 2 Example 1. Although the agitation mix of crude hexafluoride tantalate triethyl methylammonium and n-hexane was carried out, even if it existed while it had been insoluble in most and distilled off the extract layer of the back according to \*\*, hexafluoride tantalate triethyl methylammonium was not obtained at all. The result was the same, even if the quantity of n-hexane was increased to  $500\text{ ml}$  and it performed same operation.

[0037]Although reaction and refining operation were performed on the same conditions as the comparative example 1, respectively except having changed into comparative example 3 extracting solvent from n-hexane at toluene, even if it distilled off the extract layer of the back according to \*\*, hexafluoride tantalate triethyl methylammonium was not obtained at all.

[0038]

[Table 1]

表 1

	QMF・塩	抽出溶媒	収率	<sup>1</sup> H-NMR分析結果	分極測定結果
実験例 1	六フッ化タンタル酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	8.0 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 2	六フッ化ニオブ酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	7.5 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 3	六フッ化タンタル酸トリエチルメチルアンモニウム	1, 2-ジクロロエタン	7.0 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 4	六フッ化タンタル酸トリエチルメチルアンモニウム	ジクロロメタン	7.0 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 5	六フッ化タンタル酸トリエチルメチルアンモニウム	酢酸エチル	6.5 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 6	六フッ化タンタル酸トリエチルメチルアンモニウム	アセトニトリル	6.5 %	目的物のピークのみ検出	不純物ピーク検出せず
実験例 7	六フッ化タンタル酸トリエチルメチルアンモニウム	メタノール	6.0 %	目的物のピークのみ検出	不純物ピーク検出せず
比較例 1	六フッ化タンタル酸トリエチルメチルアンモニウム	アセトン	2.0 %	目的物のピークのみ検出 ピークを多数観測	不純物ピーク検出せず
比較例 2	六フッ化タンタル酸トリエチルメチルアンモニウム	ローヘキサン	0 %		不純物ピークを多数観測
比較例 3	六フッ化タンタル酸トリエチルメチルアンモニウム	トルエン	0 %		

[Translation done.]